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Annual Technical Report

PREPARATION AND CHARACTERIZATION OF
SINGLE CRYSTALS AND EPITAXIAL LAYERS OF
SILICON CARBIDE BY MOLTEN SALT ELECTROLYSIS

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The electrodeposition of silicon carbide from various molten salt systems is described. The most promising system of those studied to date is the binary Li_2CO_3/SiO_2 system with electrolysis proceeding using SiC electrodes at 1000-1050°C .

Considerable progress has been made towards optimizing the conditions used for electrodeposition. Zirconium or vitreous carbon crucibles are most

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20. favorable from the standpoint of the stability of the lithium carbonate
against decomposition. An SiO_2 concentration of 0.20 ± 0.05 appears
most favorable, with deposition proceeding at a constant potential in the
region of 0.5V. Studies aimed at closer specification of optimum
conditions are continuing.

Electrodeposited SiC is normally polycrystalline, but there is
evidence that epitaxial deposition on a single crystal α-SiC substrate
has been achieved. This observation, if confirmed by more detailed
study, would mean that the second major goal of this program has been
achieved.

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I. INTRODUCTION

Silicon carbide is a material of great interest and potential importance for semiconducting devices which can tolerate high temperatures and radiation levels. It is currently grown by a vapor transport method in a few laboratories but severe problems are encountered in obtaining reproducibly crystals of adequate size and purity for device applications.

The aim of this investigation is to develop a process for the production of layers and bulk crystals by electrolysis of molten salts. Ideally the process should produce the cubic β-phase since it occurs at temperatures much lower than those normally used to grow SiC.

Considerably progress has been made towards optimizing conditions for electrodeposition of SiC from the Li_2CO_3/SiO_2 system which has been the most successful system of those investigated. Studies of the stability of this system have helped in the selection of crucible and electrode materials. The morphology of the deposits has shown a steady improvement and there is evidence for the first time of epitaxial deposition on {0001} α-SiC substrates.

II. MOLTEN SALT ELECTROCRYSTALLIZATION OF SiC

The electrodeposition of SiC requires the simultaneous cathodic deposition of silicon and carbon under conditions where reaction to form SiC will occur. In this study sodium or lithium carbonate have been preferred as the source of carbon by the reaction

$$Li_2CO_3 \rightarrow Li_2O + C \text{ (cathode)} + O_2 \text{ (anode)}$$
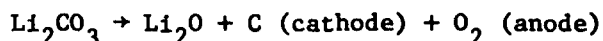
and SiO_2 or K_2SiF_6 have been used to give silicon, e.g., by the reacton

$$K_2SiF_6 \rightarrow 2KF + Si \text{ (cathode)} + 2F_2 \text{ (anode)}.$$
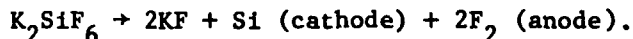
An ideal system for electrodeposition is one in which the carbonate and fluosilicate (or SiO_2) are present in high concentration. The viscosity of the melt should be low, and the melt components should all be stable at the deposition temperature so that the composition does not change appreciably during deposition. Alkali metal salts are normally preferred since deposition potentials for crystallization of the metal are relatively high.

A literature survey of the crystal growth of SiC from solution showed that temperatures below 1400°C are rarely used, although vapor growth has been achieved at approximately 1050°C. The maximum temperature for electro-deposition of SiC is determined primarily by the stability of the carbonate, which has been studied as an important factor in this investigation. A maximum temperature of 1200°C has been employed to date, the minimum temperature being 750°C since the formation of well-crystallized SiC is unlikely at lower temperatures.

III. APPARATUS

The electrodeposition of SiC has been carried out in a variety of apparatus, some of which was described in our previous reports. Of parti-cular interest is a new furnace design which permits more reliable opera-tion at relatively high temperatures (typically up to 1250°C in this study, but with a 1500°C capability). This type of furnace has been used increasingly in recent months and has led to improved results.

Figure 1 shows a diagram of the completed furnace. The heating element is made of graphite with dimensions of 11.4 cm OD and 11.1 cm high with a wall thickness of 0.95 cm. The element is slotted so that it acts as two parallel folded linear elements of length 66 cm, width 2.5 cm, and depth 0.95 cm. The element is supported on two "D" shaped graphite supports which are sections of a circle 16.5 cm in diameter. These supports, which have an overall height of 6.7 cm, have a wall thickness of 1.4 cm and have the major part of their vertical walls removed to lessen heat transfer and to allow access to the mounting bolts. The supports also act as heat shields lessening radiation to the bottom plate and are grooved on their top surface to hold a ceramic ring which insulates the two graphite heat shields. The element supports are attached to two water-cooled power feedthroughs made from copper 3.8 cm in maximum diameter and 1.3 cm diameter where they are attached to the element support. The power feedthroughs are insulated from the bottom plate by Teflon spacers and are sealed by Viton O-rings. The two graphite heat shields are 0.48 cm thick. The inner shield is 13.3 cm OD and 12.1 cm high while the other one is 16.5 cm OD and 14 cm high with a 7.6 cm opening in the top. The outer heat shield is of fused
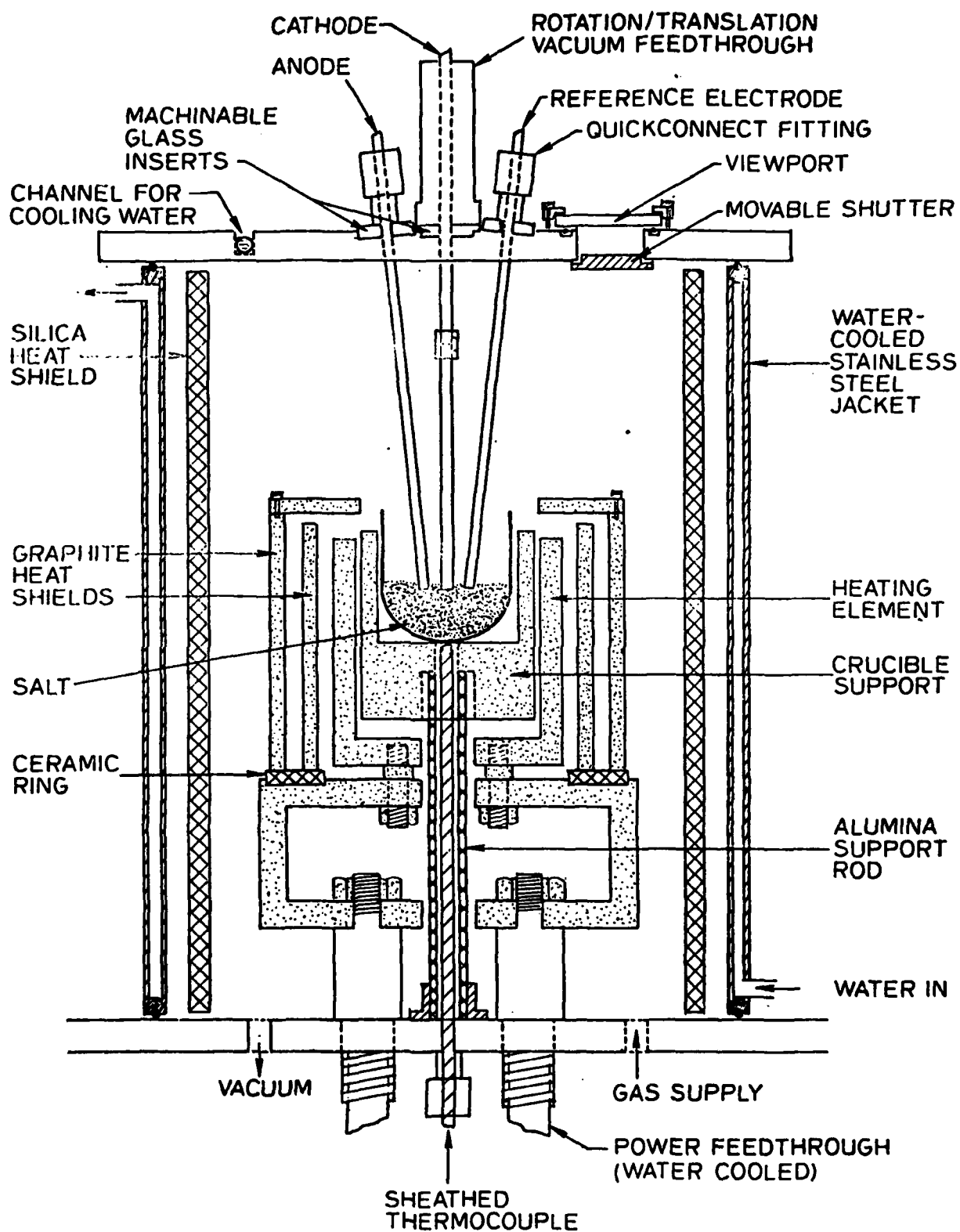
Fig. 1. Furnace used for electrodeposition
up to 1500°C (diagrammatic).

silica (22.9 cm diameter, 34.9 cm high, and 0.4 cm thick) and is surrounded by water-cooled stainless steel jacket (26.2 cm ID, 27.9 cm OD, 35.2 cm high).

The crucible is held in a graphite crucible holder which is supported by an alumina tube 1.9 cm in diameter and 17.1 cm high. The holder has an axial hole to allow a thermocouple to contact the bottom of the crucible. This thermocouple is used for both measurement and control of temperature.

The whole furnace assembly rests on a 1.3 cm thick, 32.4 cm diameter brass plate. This plate has fittings for the thermocouple and for vacuum and gas (usually argon) connections. Water cooling is provided by copper tubing (0.64 cm OD) soldered into grooves machined in the plate. This method of cooling was chosen over internally machined water channels because of its simplicity and ease of execution. The entire plate is nickel plated for corrosion resistance. The furnace is closed by a 1.9 cm thick brass plate. The plate is machined to accept three electrodes. The center electrode (cathode) passes through a rotary vacuum feedthrough (Varian), the other two electrodes pass through Quick Connect fittings. The outer electrodes are inclined at 6° to the vertical by machining a recess in the top plate. All three electrode fittings are mounted on Corning machinable glass insets to provide electrical insulation. The machinable glass is sealed to the metal using epoxy which appears to have a good lifetime if the fittings are individually cooled. A 5 cm diameter sapphire window sealed by O-rings provides a view of the interior of the apparatus. This window is protected from condensation and fogging by a movable shutter controlled through a Quick Connect fitting. This plate is cooled in the same manner as the bottom plate. Vacuum sealing of the system is provided by O-rings carried in grooves at the top and bottom of the outer jacket.

The system is evacuated by a rotary vacuum pump which is capable of bringing the manifold vacuum down to 20 μm. The furnace is normally evacuated, then a flow of inert gas introduced during deposition. The two-way valve connecting the chamber to the pump or inert gas supply is bypassed by a 1 psi relief valve to prevent excessive pressure buildup

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in the furnace. The inert gas atmosphere is admitted through a needle valve and its rate of flow is monitored by a flormeter.

A special transformer was wound which would provide 20 volts AC at 1000 amps from a 208 volt supply. The output of this transformer is carried to the furnace on leads consisting of two lengths each of 6 cm wide x 0.5 cm thick copper braid.

The input to the transformer is controlled by a Eurotherm-type 962 phase-fixed SCR unit with a capacity of 120 amps at 240 volts. This unit is controlled by a Eurotherm 919 digital temperature controller. The sensing element is a Pt-30% Rh. Pt-6% Rh thermocouple and a digital temperature display is also provided. A flow switch is used to shut down the power if the cooling water flow falls below 1.5 gallons/minute.

IV. EXPERIMENTAL

A. System $K_2SiF_6/Li_2CO_3/LiF/KF$

This system was initially considered of particular promise since silicon had been deposited so epitaxial layers from $K_2SiF_6/LiF/KF$ solutions, and carbon can be readily deposited from Li_2CO_3 alone or with addition of the LiF/KF eutectic. It was found possible to deposit SiC from solutions containing about 5 m/o K_2SiF_6 and 20 m/o Li_2CO_3 at 750°C, with deposition potentials in excess of -1.6V (versus platinum) and current densities of about 30 mA cm^{-2}. Lowering the current density in attempts to improve the morphology normally led to the complete absence of any deposit.

Problems were also encountered with reproducibility of deposition and these appeared to be associated with the presence of excess carbon in the deposit. This excess, present mainly as crystalline graphite, appeared to have an adverse effect on the morphology of the deposit. Varying the Si:C ratio over a wide range did not result, as would normally be expected, in a systematic variation in the Si:C ratio in the deposit and it was found to be extremely difficult to eliminate the excess of carbon even when the carbonate concentration in the melt was reduced to low values.

B. System $SiO_2/Na_2CO_3/NaBO_2/LiF$

The use of borate/carbonate melts for the preparation of refractory carbides was introduced by Weiss (1946) who was able to prepare carbides

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of iron, molybdenum, and tungsten by adding Fe_2O_3, MoO_3, or WO_3 to melts containing Na_2CO_3 and $NaBO_2$, with LiF added to lower the viscosity. In our work similar compositions were used with SiO_2 replacing the above oxides.

The ratio of Na_2CO_3 to SiO_2 chosen on the basis of Weiss' work was 4.2 to 1. It was confirmed that SiC could be electrodeposited from this system. The deposits contained excess carbon which was determined quantitatively by oxidation in air at 700°C, at which temperature the carbon is completely removed as CO_2 while the SiC is stable against oxidation. The ratio of Na_2CO_3 to SiO_2 was lowered systematically to 0.53 but the concentration of excess graphite was found to be remarkably insensitive to the carbonate to silica ratio in the melt (see Table I). As in the case of the K_2SiF_6/Li_2CO_3 melt, the morphology of the deposit and its crystallinity (as determined by x-ray powder photography of the deposited material) were generally poor.

C. System Li_2CO_3/SiO_2

During approximately the last nine months of the program, work has been concentrated on the binary system Li_2CO_3/SiO_2 which has given the most promising deposits. Lithium carbonate melts at 723°C and, according to the Handbook of Chemistry and Physics (CRC Press), decomposes at 1310°C at one atmosphere pressure. In practice, however, this decomposition temperature is greatly lowered by contact with carbon or metals. The temperature range over which deposition can proceed is therefore limited at its upper boundary by the stability of the carbonate, which depends on the container and electrode materials. The lower limit is fixed by the requirement that the $SiO_2:Li_2CO_3$ ratio be sufficiently high for the formation of SiC without excess carbon, and the crystal quality of the deposit is likely to decrease with decrease of temperature rather than the reverse. A study of the stability of Li_2CO_3/SiO_2 melts was therefore undertaken as the first stage of a systematic investigation of the influence of the various operating parameters on the electrodeposition of SiC from this system. While this study is by no means complete, the results obtained to date are given the highest priority in this report.

1. Crucible Material

The influence of the crucible material on the decomposition of lithium carbonate was studied by two methods. The simplest was by the use of thermogravimetric analysis using the TGA attachment to a Du Pont DTA/TGA apparatus. Fig. 2 shows the combined traces obtained with different crucible materials. In each case the evolution of CO_2 from Li_2CO_3 occurs a little above its melting point (723°C) and increases as the temperature is raised. The weight of Li_2CO_3 is different in each case and so the weight loss data should be referred to constant weight of Li_2CO_3. However, even the comparison at constant Li_2CO_3 is not quantitatively valid since the area of contact between powder and crucible will influence the decomposition kinetics. The data do suggest, however, that vitreous carbon is the most suitable crucible material.

The alternative procedure used to compare various crucible materials consisted of heating a weighed sample of lithium carbonate rapidly to 1000°C, holding it at this temperature for an hour, then cooling rapidly to room temperature and re-weighing. The results of this study are given in Table II. The data confirm that vitreous carbon is the best crucible material in terms of stability of the carbonate, but these crucibles were covered by a large number of very fine cracks, suggesting local reactivity. In addition, failure of the crucibles always occurred during cooling and occasionally during the heating stage. In one case the melt ran out through a crack in the crucible, causing extensive damage to the furnace. Because of this cracking of vitreous carbon, zirconium crucibles have been preferred for later studies. The zirconium contamination in the deposits has not yet been determined, but the melts show no traces of discoloration due, for example, to dissolution and reduction of zirconium oxides.

Fig. 3(a) illustrates the influence of the silica addition on the stability of Li_2CO_3. It was expected that the SiO_2 would react with Li_2CO_3 completely to produce lithium silicate:

$$Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2 \uparrow \qquad (1)$$
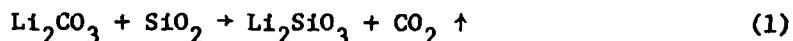
This reaction (or the alternative formation of Li_2SiO_5 or Li_4SiO_4) cannot be followed quantitatively from the TGA traces because of the parallel
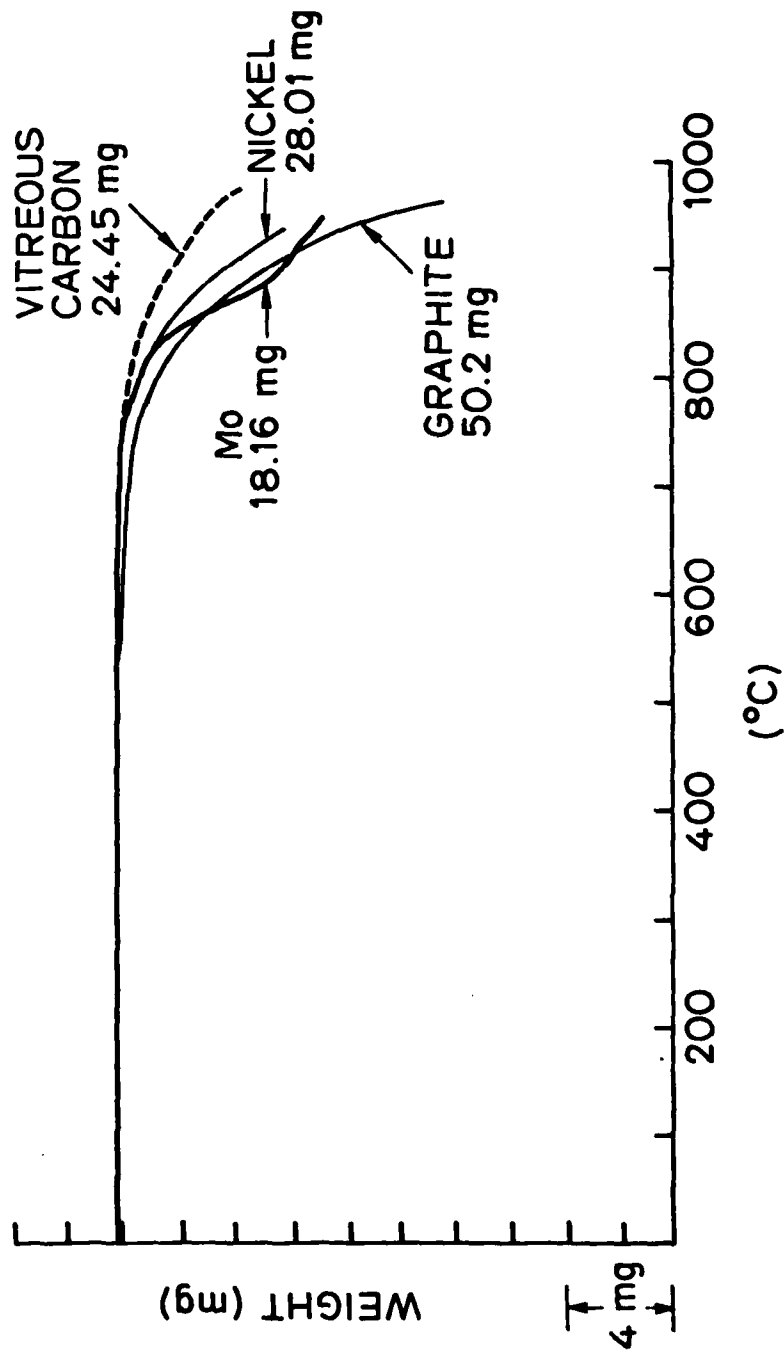
Fig. 2. Thermogravimetric traces showing weight loss of lithium carbonate versus temperature for various crucible materials. The weight of Li_2CO_3 is shown in brackets. (1 div = 2 mg)

mg

Li$_2$CO$_3$
(28.83 mg)

20% SiO$_2$
80% Li$_2$CO$_3$
(18.44 mg)

30% SiO$_2$
70% Li$_2$CO$_3$
(28.89 mg)

4 mg

200   400   600   800   1000

(°C)

WEIGHT (mg)

28

24

20

16

12

8

4

0

Li$_2$CO$_3$
ONLY

0.8 Li$_2$CO$_3$
+ 0.2 SiO$_2$

0   200   400   600   800   1000
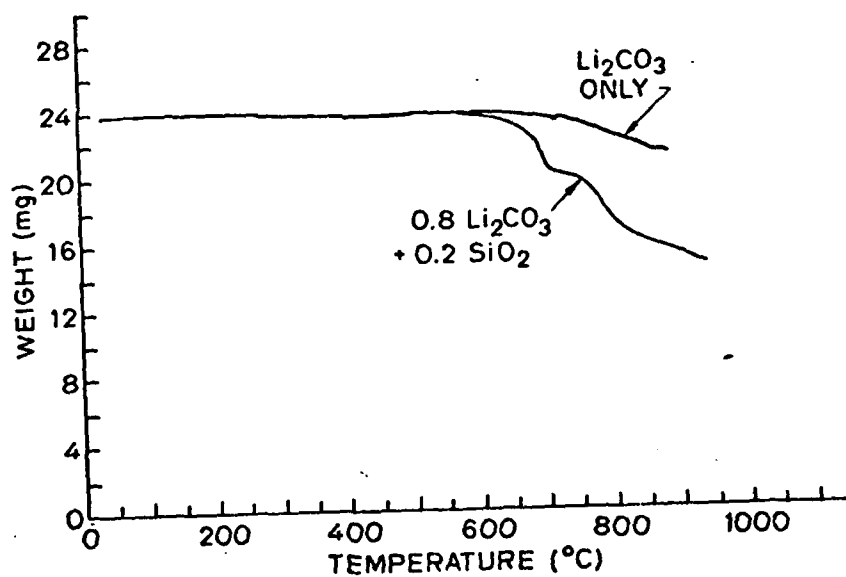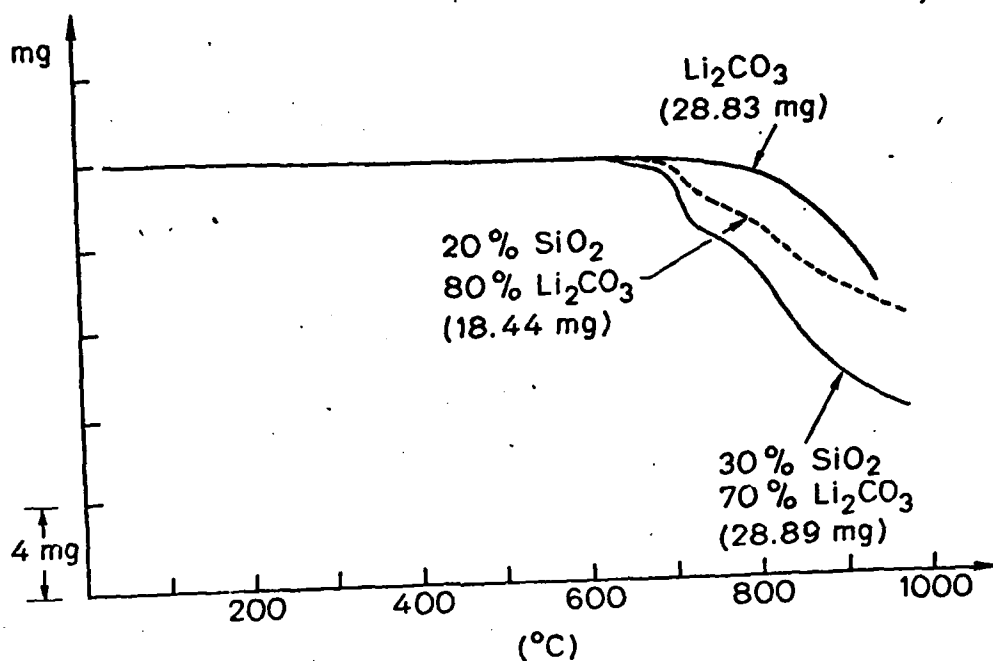
TEMPERATURE (°C)

Fig. 3. Thermogravimetric traces showing
the influence of SiO$_2$ on the decom-
position of Li$_2$CO$_3$. (a) Nickel
crucible (b) Glassy carbon crucible.

decomposition of the Li_2CO_3 itself:

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \uparrow \tag{2}$$

If the traces for Li_2CO_3 and 0.7 Li_2CO_3: 0.3 SiO_3 in Fig. 3(a) are compared, the difference between the two curves is approximately the 6.36 mg which would be expected according to Eq. (1). The SiO_2 addition appears to lead to decomposition of Li_2CO_3 some 100°C below its melting point, the discontinuity in the weight versus temperature trace at the melting point of Li_2CO_3 being well defined in the diagram. This effect is not so marked when a vitreous carbon crucible is used (Fig. 3b) but extensive TGA data have not been obtained in this case because of the difficulty of fabricating very small crucibles in vitreous carbon. (Those used in this investigation were cut from the corners of rectangular crucibles by slicing manually held crucibles with a diamond wheel).

2. Electrode Materials

In the early stages, a cathode other than SiC was preferred so that the synthesis of SiC could be demonstrated. Nickel was chosen for convenience and because of its relatively low reactivity with the melt. Nickel suffers from the disadvantage that it reacts with silicon to form nickel silicides, but the concentration of silicides in the deposits was low. The successful synthesis of SiC in this system was demonstrated using a nickel cathode and graphite anode.

Silicon was also used as cathode but reacts rather rapidly with the melt. The most appropriate choice of electrodes appears to be silicon carbide itself. Polycrystalline SiC was obtained from the RIC/ROC Chemical Company and found to be very stable against chemical attack by the melt. "Globar" heating element material, which is mainly SiC but with a binder, was found to be unsuitable because of its high reactivity. An extensive search for single crystal SiC at reasonable cost led eventually to the location of a retailer who can supply plate-like crystals of 6H polytype over 1 cm^2 in area. These crystals are formed as an accidental by-product of the formation of SiC powder for abrasive applications, and examples of a cluster of crystals and individual crystals broken from a polycrystalline matrix are shown in Fig. 4. The matrix is used to locate the material in
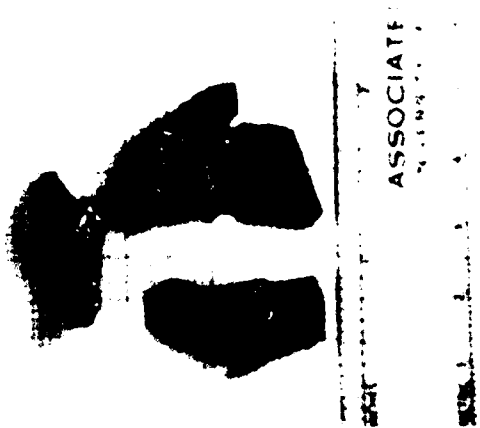
Fig. 4. (a) Cluster of SiC crystals
(b) Individual SiC crystals used as
substrates for electrodeposition.

a graphite holder, the single crystal portion being immersed in the melt to act as cathode. During deposition the melt tends to creep up the crystal and support because of its strong wetting action, and this makes an exact specification of current density difficult. This action also leads to contamination of the deposited material with nickel from the wire used to secure the crystal, but this problem should be alleviated by the use of zirconium wire or an all-graphite support. Polycrystalline SiC is used as the anode.

3. Current-Voltage Dependence

Figure 4 shows a comparison of the dependence of current on voltage for various melts at 1000°C with nickel crucible and SiC electrodes. The melts in each case were freshly prepared and were heated in vacuo for several hours at 300°C and allowed to homogenize at 1000°C for about one hour. The graphs are almost linear in each case and show no evidence of minimum deposition potentials for either carbon or silicon. The most striking observation is the large increase in current with SiO_2 addition, which suggests that the silicate ions are relatively mobile. Although it is not possible to reproduce exactly the area of electrode immersed, the traces suggest that silicon will be deposited relatively easily and this result is favorable since problems were encountered in the previously-used systems in avoiding an excess of graphite.

4. Optimization of Electrodeposition Conditions

Considerable progress has now been made towards the selection of optimum operating conditions for SiC electrodeposition. Although these studies are far from complete, significant improvements in reproducibility and in the morphology of the layers have recently been achieved. This section is a summary of recent results aimed at establishing optimum deposition conditions.

a. Temperature

To date it has not been found possible to electrodeposit SiC at temperatures below 950°C. This limit is probably set by the tendency of lithium silicates to deposit on the electrodes due to the cooling effect

of thermal conduction along the graphite rods. This thermal deposition of lithium silicate is clearly more likely to occur at lower temperatures and at higher SiO_2 concentrations. The lower temperature limit for electrodeposition may therefore be composition-dependent and is probably not a fundamental effect associated with the reaction between electrodeposited silicon and carbon.

The highest temperature at which SiC deposition has been achieved is about 1225°C. This limit was mainly dictated by practical considerations and the influence of temperature will be investigated in more detail with a fixed melt composition. It is, however, encouraging that the rate of CO_2 loss at this temperature is not so rapid that SiC deposition becomes impossible.

Unless otherwise specified, all experiments reported below were performed at melt temperatures between 1000°C and 1050°C.

b. Deposition Potential

The voltammograms of Fig. 5 do not provide useful information on the choice of operating potential difference between anode and cathode. Stability considerations (Huggins and Elwell 1977, De Mattei and Feigelson, 1978) normally favor a low current density and our earlier work at $T \sim 750°C$ was handicapped by the apparent failure of SiC to deposit unless large current densities were used. High current densities ($\gtrsim$ 50–100 mA cm^{-2}) frequently result in very irregular morphologies (e.g., dendritic growth) with high concentrations of solvent inclusions. However, Fig. 6 shows a cross section of a 200 μm thick layer of SiC which was deposited at a constant potential of -0.95V (vs SiC) at 1226°C with a current density $\sim$ 500 mA cm^{-2}. Although the surface morphology of this layer is irregular, the absence of detectable solvent inclusions is encouraging.

Better surface morphologies have been obtained at a deposition potential of -0.5V (vs SiC) and this value has been preferred for investigations of the influence of composition on the quality of the electrodeposit. The corresponding current density is typically from 30 to 50 mA cm^{-2}. The deposition time is normally 90 minutes.

c. Concentration of SiO_2

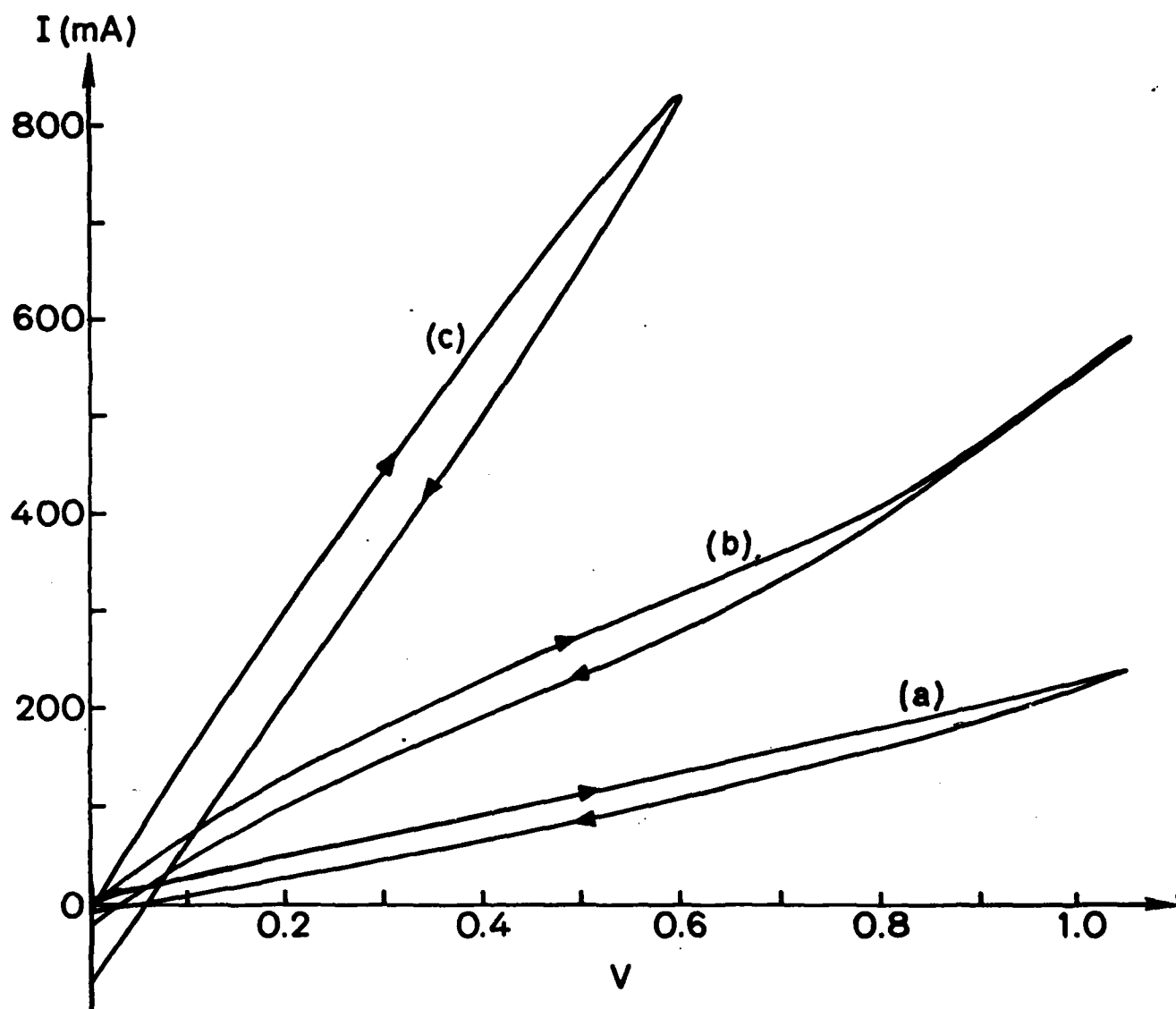The earliest experiments were made with melts of composition

Fig. 5.   Slow scan voltammograms using SiC
anode and cathode at 1000°C
(a) Li_2Co_3 only (b) 0.9 Li_2CO_3 +
0.1 SiO_2 (c) 0.8 Li_2CO_3 + 0.2 SiO_2.

Fig. 6. Cleaved cross section of SiC deposit
on SiC at 0.95V (vs SiC) and
$\sim$ 500 mA cm^{-2}.

0.6 Li_2CO_3; 0.4 SiO_2, the rather high SiO_2 concentration being used to avoid excess graphite in the deposit. Melts containing such high concentrations of SiO_2 are very viscous at 1000-1100°C and the SiO_2 concentration x in the system (1-x) Li_2CO_3 x SiO_2 has been varied in the range $0.1 \lesssim x \lesssim 0.3$ in an attempt to find an optimum composition. A comparison of the surface morphology of deposits for different values of x is given in Figures 7-9.

Figure 7 shows a deposit from a melt with x = 0.10 which is rather irregular in texture and shows poorly-formed grain structure. Although this deposit was made at 0.85V, the poor morphology indicates that this concentration of SiO_2 is below the optimum range. Figure 8 shows two examples of deposits from melts with x = 0.20 under "standard" conditions (1000-1050°C; 0.5V vs SiC; 35-70mA on over 1 cm^2 area). The surface of Fig. 8(a) is irregular but shows a strong tendency towards textured or even epitaxial growth. Fig. 8(b) shows a polycrystalline sample but with well-developed grains up to 100 μm in diameter (some traces of melt are adhering to the surface of this deposit). Figure 9 shows the surface of a deposit from a melt with x = 0.30 under nominally identical conditions to those used in the case of Fig. 8(b). Although the grains in this case are up to 200 μm in diameter, there are also many small grains and the surfaces of the grains are much rougher than in the x = 0.2 case. Although the data obtained to date are not conclusive, Figures 7-9 are representative of a range of deposits, and we believe that the optimum melt composition is in the range x = 0.20 ± 0.05 and are concentrating our present efforts on this composition region.

d. Fluoride Addition

Since the viscosity of Li_2CO_3/SiO_2 melts at T ∿ 1050°C is high for electrodeposition, NaF was added in a concentration of about 10 wt % in one experiment in order to lower the melt viscosity. The volatility of NaF was found, however, to be excessively high at T ∿ 1050°C and damage occurred to the silica heat shield surrounding the furnace element. An additional detrimental effect was the occurrence of fine whisker-like deposits on the SiC grains. The nature of these whiskers has not been established, but fluoride additions have not been used subsequently. LiF has a lower vapor pressure and could be used as alternative to NaF but

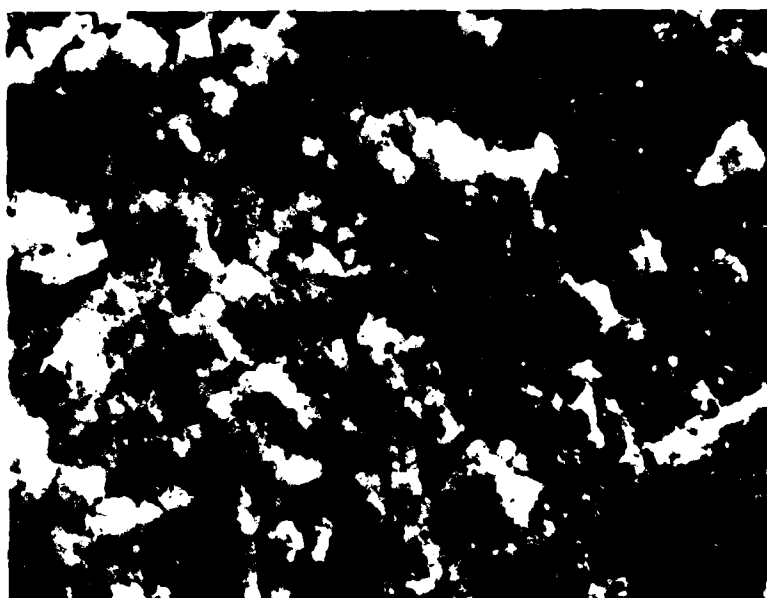Fig. 7. Surface of SiC electrodeposit from
melt of composition 0.9 Li_2CO_3,
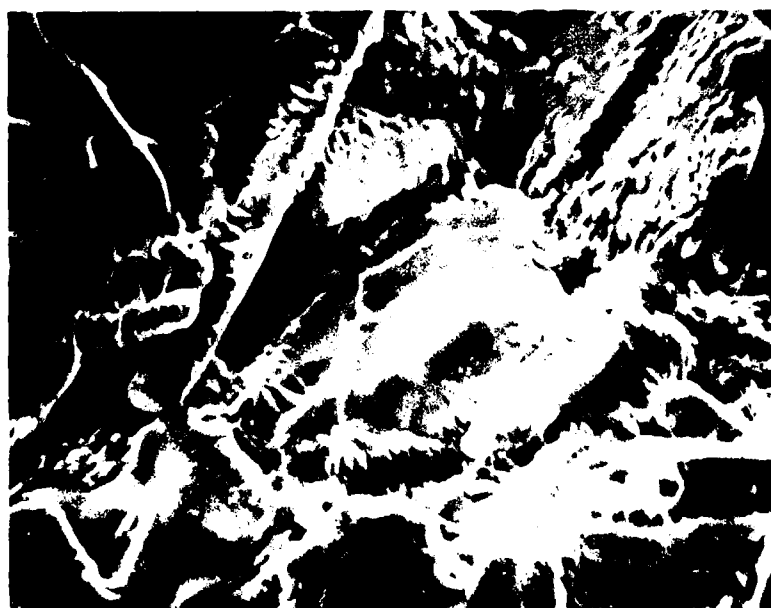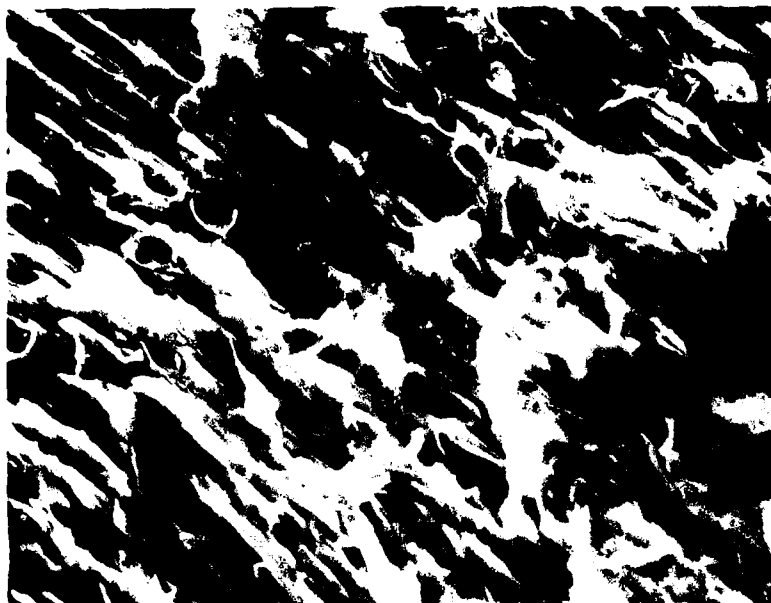0.1 SiO_2. Deposition potential 0.85V;
deposition time 3 hrs. (800x).

Fig. 8. SiC electrodeposits from melts of
composition 0.8 Li_2CO_3. 0.2 SiO_2 at
0.5V (a) deposition time 3 hrs.
(2000x) (b) deposition time $1\frac{1}{2}$ hrs
(500x).

Fig. 9. SiC electrodeposit from melt of com-
position 0.7 Li_2CO_3. 0.3 SiO_2
(200x).

adhering traces are difficult to remove from the deposit because of its low solubility in water or acids.

5. Characterization

Detailed characterization of electrodeposited SiC has not yet been performed since improvements in the quality of the best deposits are being made fairly rapidly at the present stage. Attempts have been made, however, to determine, using x-ray crystallography, the polytype of polycrystalline SiC deposited on polycrystalline substrates. The d-spacings and intensity values of a typical powder deposit are listed in Table III. Also shown for comparison are the literature data for several of the more common polytypes. It can be seen from the comparison of two sets of literature data for the $\alpha(6H)$ polytype that large discrepancies occur between different workers and presumably between different samples.

The presence of extra lines show fairly convincingly that the material deposited is not 2H, 4H, or β (cubic) SiC. Similarly, strong or medium intensity lines are present in both 15R and 33R powder patterns which do not appear in our data, e.g., d = 2.40 and 2.32 (15R) and d = 2.09, 2.00, 1.69, and 1.64 (33R). It is therefore concluded that the material deposited in our experiments is of the relatively common $\alpha(6H)$ type, the agreement between our data and that of the two patterns taken from the literature being about as good as that between the two sets of literature data.

Deposits on α-SiC substrates appear to be epitaxial or strongly textured. Figure 10 shows a back reflection Laue photograph of an SiC deposit on a {0001} SiC substrate under conditions described above (see Fig. 8(a)). The Laue photograph shows clearly the hexagonal symmetry and no traces of rings which would be expected from a randomly oriented poly-crystalline deposit. (The layer deposited was about 50 μm thick and so would be expected to contribute to the diffraction pattern). Although the evidence of Fig. 10 is not sufficient by itself to justify the assumption that the SiC layer deposited was epitaxial, it is consistent with epitaxy.

D. Other Systems Studied

The system Rb_2O/SiO_2 is of interest since the drop in liquidus temperature on adding the alkali metal oxide to SiO_2 is more rapid than
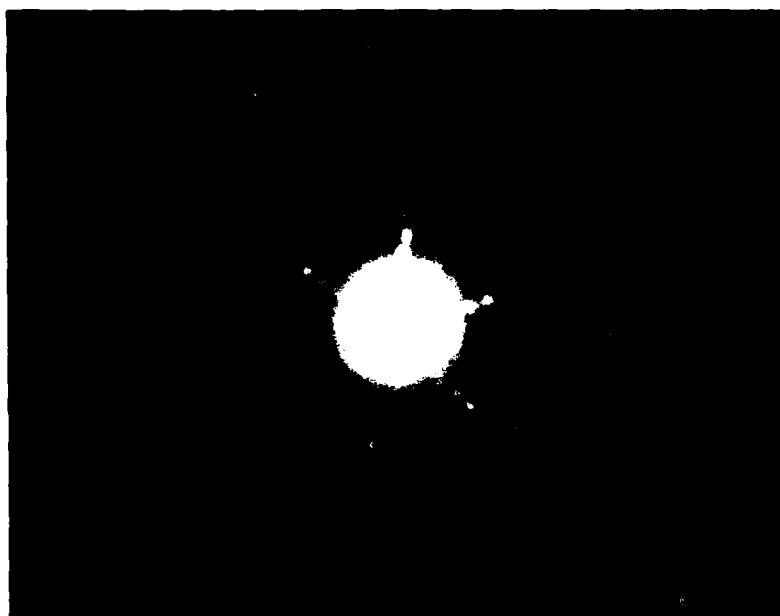
Fig. 10. Back reflection Laue photograph of
SiC deposit on {0001} α-SiC sub-
strate.

for any other oxide. Attempts were made to deposit Si from a melt in which Rb_2CO_3 was presumed to react to completion with SiO_2 and to deposit SiC from a similar melt to which Na_2CO_3 was added. Only a trace deposit was obtained, however, which was insufficient for chemical analysis.

Deposits of silicon have been obtained from the $NaCl/K_2SiF_6$ eutectic at 600-750°C. Again attempts were made to obtain SiC by adding carbonate, both Li_2CO_3 and Na_2CO_3 being used. The presence of the carbonate appeared to have an adverse effect on silicon electrodeposition, and in no case was SiC observed in the deposit. Attempts to deposit SiC from a melt containing K_2SiF_6, $BaCO_3$, and NaCl were also unsuccessful.

The system $K_2O/MgO/SiO_2$ has a series of low-melting eutectics, the composition of lowest melting point having a liquidus temperature below 800°C. Electrolysis at 1000°C of a melt of molar composition $3K_2O$; 1 MgO; 0.5 SiO_2; 1 Li_2CO_3 yielded silicon with salt inclusions but no trace of carbon. The same melt, but without Li_2CO_3 was found to attack the graphite anode strongly with significant vaporization. Further study of a $K_2CO_3/MgO/SiO_2/Li_2CO_3$ melt led to the conclusion that potassium is the primary product on electrolysis, as in the case of K_2O/SiO_2 melts which have been investigated previously.

IV. CONCLUSIONS

The Li_2CO_3/SiO_2 system appears capable of yielding good quality layers of SiC by electrodeposition. The deposits are of α-SiC and there is evidence of epitaxial deposits on {0001} α-SiC substrates at least over part of the sample area.

Progress has been made towards optimizing the deposition parameters from this system. The best deposits to date were made from a melt of composition 0.8 Li_2CO_3, 0.2 SiO_2 at 1000-1050°C with a constant potential of 0.50 V applied for 1½-3 hours. The crucible used was zirconium and SiC was used for both anode and cathode.

The melt loses CO_2 at an initial rate of about 10% per hour. Although this rate falls with time, the stability of the melt appears at present to be the major limitation in producing bulk crystals.

Further studies aimed at optimizing the deposition conditions are

in hand at present. More detailed characterization of the deposits will
be performed and experiments aimed at improving the purity of the deposits
(especially by pre-electrolysis) will be carried out.

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TABLE I. DEPOSITIONS FROM SiO_2/Na_2CO_3/$NaBO_2$/LiF SYSTEM

	Melt Composition (m/o)				Ratio Na_2CO_3 : SiO_2	Deposit Potential V_d (V)	Deposit
	$NaBO_2$	LiF	Na_2CO_3	SiO_2			
(1)	13.8	70.3	12.9	3.1	4.1	.75	Cohesive, poor morphology; 55% excess carbon
(2)	14.6	74.8	7.3	3.3	2.2	.50	Less cohesive than (1) poor morphology ; 50% excess carbon
(3)	14.9	75.5	4.4	5.2	.85	1.21	Smooth, flaky, poorly cohesive; low efficiency; 48% excess carbon
(4)	15.1	76.7	2.8	5.3	.53	1.4	Powdery deposit, poor crystallinity 50% excess carbon
(5)	13.5	76.2	6.7	3.5	1.9	1.1	Li_2SiO_3; no SiC.

TABLE II. WEIGHT LOSS OF LITHIUM CARBONATE IN VARIOUS CRUCIBLES

Crucible Material	Weight Loss (%)	Reactivity
Vitreous carbon #1	12.5	Low but cracked.
Vitreous carbon #2	12.3	
Vitreous carbon #3	8.5	
Zirconium	16.3	Low
Silicon nitride	50.9	High
Titanium carbide	50.9	High
Niobium	65.0	High
Magnesium oxide	85.1	Very high

TABLE III. INTENSITY DATA FOR SiC X-RAY DIFFRACTION PATTERNS

d(Å)	Experimental Data	α(6H) *	+	β	2H	4H	15R	33R
2.63	25	50	70	–	60(2.67)	40(2.67)	40	50
2.60	–	20	~	–	–	–··	–	–
2.57	15	20	–	–	–	50	70	–
2.51	100	100	100	100	100	40	70	100
2.48	–	20	20	·–	–	–	–	–
2.40	–	–	20	–	–	–	60	–
2.36	30	40	10	–	80	50	–	60
2.34	–	30	~	–	–	–	50	–
2.18	30	20	10	10	–	–	10	30
2.15	–	20	~	–	–	–	–	–
2.09	–	–	~	–	–	30	30	20
2.00	–	–	30	–	–	–	10	20
1.865	15	–	~	–	–	–	–	20(1.69)
1.84	20	–	~	–	20	20	–	20(1.64)
1.60	–	–	~	–	–	40	50	–
1.55	10	50 ⎫		–	–	60	–	30
1.54	15	50 ⎭ 80		60	–	–	90	80
1.50	–	–	30	–	–	–	–	10
1.42	85	20+20	30+20	–		50	40	30+30
1.31	85	50	70	60	–	70	80	70
1.29	–	–	–	–	–	40	20+20	30
1.26	10	10	30	10	–	30	20	30

*Thibault Am. Min. 93 (1948) 588.
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